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In situ NH_2-functionalized graphene oxide/SiO_2 composites to improve Cu(II) removal from ammoniacal solutions

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HIGHLIGHTS

- Amino groups were in situ grafted on the GO/SiO_2 composites in ammoniacal media.
- A special adsorption behavior for Cu(II) removal was elucidated.
- The special affinity of amino groups with Cu(II) is beneficial for the adsorption.
- The maximum adsorption capacity of Cu(II) is 158.9 mg g^{-1} at equilibrium conditions.

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ABSTRACT

A special adsorption manifestation for Cu(II) removal from ammoniacal solutions was elucidated. In this process, the graphene oxide/SiO_2 composites (GO/SiO_2) were prepared by a facile method, and the amino groups were successfully grafted on the surface of GO/SiO_2 through an in situ functionalized reaction in the ammoniacal media. The composites were thoroughly characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared (FT-IR), Raman and X-ray photoelectron (XPS) spectroscopies. The spectral analyses proved that the amino groups can be in situ generated through the reaction between ammonia molecules and functional groups on the surface of composites. The results indicate that the NH_2-functionalized GO/SiO_2 composites are beneficial for the adsorption of Cu(II) due to the special affinity of amino groups with Cu(II). The effects of solution pH, mass percentage of GO in composites and temperature have been discussed by batch adsorption experiments. The experimental data can be well fitted with the pseudo-second order kinetics and Freundlich isotherm models. The maximum adsorption capacity of Cu(II) is 158.9 mg g^{-1} at equilibrium conditions. In addition, thermodynamics study confirmed the endothermic nature of Cu(II) adsorption, and the adsorption mechanism was discussed. Hence, the GO/SiO_2 composites have great potential for the efficient removal of Cu(II) from ammoniacal solutions.

1. Introduction

Heavy metals wastewaters pose a serious threat to human beings and environments because of their toxicity and accumulation characteristics in nature. It has become very urgent to find the appropriate solutions to remove heavy metals from wastewaters [1–3]. Copper is one of the toxic heavy metals discharged by various industries, such as printed circuit boards (PCB), electroplating, dye painting, textile and paper industries. Among them, the treatments of PCB and dye painting wastewaters are the most tough problem due to the fact that copper exists in the ammonia-bearing industrial effluents [4,5]. In the ammoniacal media, ammonia molecules replace the inner-sphere coordinated water molecules of hydrated copper ions, thus the coexisted copper ammonia species and their strong stability can evidently depress the Cu(II) removal. Thus, after treating with the general precipitation method, several hundred ppm of copper can still present in the ammoniacal wastewaters and is deleterious for the environments.

In recent years, various contaminant remediation technologies have been developed for the elimination of copper and other toxic metals from wastewaters, such as ion exchange, chemical precipitation, reverse osmosis, membrane separation and adsorption. Adsorption is one of the promising and extensive methods, because of its high efficiency, stability characteristics, easy handling as well as availability of diverse adsorbents [6–10]. Some traditional adsorbents have been used for toxic metals removal, including activated

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carbon [11,12], minerals [13] and so on. However, these adsorbents have the weak affinity with heavy metal ions and the evident disadvantage of low adsorption capacity for heavy metal removal. The rapid development of nanomaterials provides a good alternative to solve these problems, which benefiting from their higher specific surface area and sequestration characteristics [9,14]. Carbon materials are a kind of traditionally and widely used engineering adsorbents for the wastewater treatment [2,15]. Especially, graphene oxide (GO), an oxidized derivative of graphite, presents a good adsorbent performance for heavy metals, radioactive elements and rare earths in various wastewaters [16–20], because of the abundant functional groups on its surface, such as hydroxyl, epoxide, carbonyl and carboxyl groups. However, due to the π–π interaction, the aggregation features of two-dimensional GO nanosheets can restrict the active sites to be exposed. Although sonochemical approach is generally used to prevent the GO aggregation and tune the surface chemistry of graphene oxides [21], the GO-based composites with metal/nonmetal oxides can be generally considered as the promising candidates for toxic ions adsorption [3,6]. Considering the low cost, non-toxicity and chemical stability of SiO_2, the GO/SiO_2 composites exhibit a great potential as adsorption and catalysis materials. In addition, the support SiO_2 has a good compatibility in the ammoniacal media due to its low solubility, thus favoring for the absorbent stability.

Although there are abundant surface chemistry on GOs [22], it is well known that the GOs decorated with nitrogenous ligands can exhibit a stronger adsorption ability due to their special coordination and affinity with metal ions [7,23,24]. There is generally involved a beforehand functionalized processes to modify the surface properties of GOs through various methods, including chemical crosslinking, chelation and graft. Xing et al. [25] found that the GOs crosslinked with NH_2-rich polymers can be used for Cu(II) removal with the high adsorption capacity. Luo et al. [26] found that GOs can selectively remove Pb(II) with the high capacity through linking with amino siloxane oligomer. For the graphene oxide-supported polyaniline composites, Sun et al. concluded that the chemical affinity of nitrogen-containing functional groups for radionuclides is stronger than that of oxygen-containing functional groups [24]. Moreover, some typical amino ligands including ethylenediaminetetraacetic acid [7], ethylenediamine triacetic acid [23] and amino acids [27] can be chemically grafted to the host adsorbents to markedly improve the toxic metal removal. Therefore, optimizing the surface properties of GOs by amination is preferred for metal adsorption.

Unlike the general amination process of GOs, herein in view of the specific ammoniacal media, an in situ NH_2-functionalized process was proposed to introduce amino groups on the surface of graphene oxide/SiO_2 composites. The composition of GO/SiO_2 composites was optimized by consideration of the mass percentage of GO in composites. And the IR, Raman and XPS spectroscopies have been used to clarify the in situ generated amino groups on the GO/SiO_2 composites. The Cu(II) adsorption abilities of GO/SiO_2 composites from the ammoniacal media were evaluated at different feed pH conditions and temperatures. Meanwhile, the Cu(II) adsorption mechanism was studied through the adsorption kinetics and isotherm analyses.

2. Experimental

2.1. Reagents and chemicals

Natural graphite powder (average particle size is 40 μm), copper sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$), tetraethyl orthosilicate (TEOS) and all other chemicals were used without further purification. Deionized water (Millipore MilliQ System, 18.2 $M\Omega\ cm^{-1}$) was used in all experiments.

2.2. Preparation of GO/SiO_2 composites

Graphene oxide was synthesized via the modified Hummers' method. Firstly, under the ice bath condition, 10 g graphite powders and 5 g $NaNO_3$ were mixed with 230 mL concentrated H_2SO_4 and stirred for 30 min. Subsequently, 30 g $KMnO_4$ was added slowly with continuous stirring. After the mixture was stirred for 30 min at 35 °C, 460 mL deionized water was added dropwise under vigorous stirring. The reaction temperature was rapidly increased to 98 °C and kept for 40 min until the color of mixture was changed from sepia into luminous yellow. Subsequently, 30% H_2O_2 was added into the mixture to reduce the residual MnO_4^- anions. Finally, the product was purified and washed with 5% HCl and deionized water for several times until the solution was neutral. The as-prepared GO was dried at 60 °C in vacuum after centrifuging.

Silica particles were synthesized as follows: TEOS (50 mL) and ethanol (100 mL) were completely mixed in 100 mL DI water. After 100 mL ammonium hydroxide was added, the mixed solution was stirred for 2 h at 30 °C. Finally, the white suspension was acquired through centrifuging. The gel was dried at 60 °C in vacuum and calcined at 500 °C for 3 h to obtain the SiO_2 particles.

GO/SiO_2 composites were prepared in a water/alcohol mixed solution. Briefly, as-obtianed GOs and SiO_2 particles were re-dispersed in 1:1 ethanol aqueous solution, which was stirred and refluxed for 4 h at 95 °C. Then, the centrifuged products were dried at 60 °C in vacuum for 24 h. Finally, a series of GO/SiO_2 composites were obtained with different weight percentages of GO in the GO/SiO_2 composites (20 wt%, 50 wt% and 80 wt%) by the same method, named as GOS1, GOS2 and GOS3, respectively.

2.3. Characterization methods

The morphologies of GO/SiO_2 composites were characterized by scanning electron microscopy (SEM, JSM-6360LV). The X-ray diffraction (XRD, D/Max2250, Rigaku Corporation, Japan) analyses were performed with a nickel-filtered Cu Kα radiation (λ = 1.5406 Å). The diffraction angles were ranged from 10° to 80° with a rate of 1.0° min^{-1}. The Fourier transform infrared (FT-IR) spectra of samples were recorded in KBr pellet at room temperature using a Thermo Fisher Nicolet 6700 FT-IR spectrophotometer, with a resolution of 4 cm^{-1} in the range from 400 to 4000 cm^{-1}. The Raman spectra were obtained from a Renishaw inva confocal Raman system with a 532 nm excitation laser. The surface chemical information of simples was measured by a XPS (X-ray photoelectron spectroscopy) spectrometer (K-Alpha 1063, Thermo Fisher Scientific) using monochromatized Al Ka (1486 eV) radiation. Specific surface areas of the adsorbents were determined by nitrogen adsorption and desorption at 77 K using an ASAP 2020 (Micromeritics) volumetric adsorption analyzer.

2.4. Batch adsorption experiments

The stock solution of 100 mmol L^{-1} Cu(II) was prepared by dissolving a certain amount of $CuSO_4{\cdot}5H_2O$ in deionized water. The different concentration of Cu(II) solutions were prepared by diluting of the stock solution in 100 mL of 0.1 mol L^{-1} $(NH_4)_2SO_4$. The pH of Cu(II) solutions was adjusted to the desired value from 4.5 to 10.5 using sodium hydroxide and sulfuric acid. All batch adsorption experiments of Cu(II) on GO/SiO_2 composites were carried out by shaking the Cu(II) solutions containing 0.5 g L^{-1} adsorbent in a 20 mL glass bottle at 298 K (400 rpm for 4 h). Other parameters including initial Cu(II) concentration (0.2–2.5 mmol L^{-1}), contact time (0–5 h) and temperatures (293–313 K) were studied at the pH 8 to evaluate the isotherm, kinetics and thermodynamics of Cu(II) adsorption. The suspensions were separated by centrifuging.